UNIVERSITI PUTRA MALAYSIA

ENHANCING TENSILE PROPERTIES OF CARBON FIBER-REINFORCED POLYPROPYLENE COMPOSITE USING CARBON NANOTUBE COATING

SHARIFAH MAZRAH BINTI SAYED MOHAMED ZAIN

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By

SHARIFAH MAZRAH BINTI SAYED MOHAMED ZAIN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

November 2009

DEDICATION

I dedicate this thesis to my beloved husband and twin daughters,
with love…

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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November 2009

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Carbon fibers, when used without any surface treatments, will produce composites with low interlaminar shear strength (ILSS) which attributed largely to weak bonding between the fiber and the matrix. CNT-coating treatment was conducted to improve carbon fiber-matrix interfacial bonding. This treatment was done by growing carbon nanotubes (CNTs) directly on carbon fibers using chemical vapor deposition (CVD) to create CNT-coated carbon fibers. The objectives was to study the microscopic morphology of CNTs formation on the surface of carbon fibers at various treatment conditions, to study the interfacial shear strength (IFSS) of CNT-coated carbon fibers, tensile properties and thermal stability of CNT-coated carbon fiber composites as well as comparison with untreated and commercial carbon fibers. The CNTs were produced by a benzene-ferrocene gas reaction inside a high temperature tube furnace. The reaction temperature, the carrier gas flow rate and weight of ferrocene were varied at 700 ^{o}C, 800^{o}C and 900^{o}C; 100 ml/min and 300 ml/min; 0.3 g, 0.5 g and 1.0 g respectively and the reaction time for CNT growth was set at 30 minutes. The microscopic morphology of CNTs formation on the surface of carbon fibers was

observed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) before it was fabricated into composites. The composites were prepared by melt blending with polypropylene (PP) at different fiber content of 2, 4, 6, 8, 10 and 12 wt. %. It showed that CNTs were successfully grown on carbon fibers at reaction temperature of 800^{o}C and 900^{o}C. Interfacial shear strength of CNT-coated fibers improved up to 499% compared to untreated fibers. Tensile properties increased with the increase of fiber loading from 2 wt. % - 10 wt. % and decreased at 12 wt. % fiber content. With addition of 10 wt. % of CNT-coated CFPP composites, the tensile strength and modulus increased up to 36% and 85%, respectively. CNT-coated CFPP composites were more resistant to deformation, but had lower strength when compared with commercial CFPP composites. The thermal stability of CNT-coated CFPP composites showed an increment compared to the untreated CFPP composite. As conclusion, CNT-coating treatment using parameters treated at reaction temperature of 800^{o}C; 300 ml/min hydrogen flow rate and 1.0 g of ferrocene showed the most amounts of CNTs with fewer impurities which also exhibited the best performance in IFSS, tensile properties and highest onset degradation temperature, 325^{o}C making it the best designation for this CNT-coating treatment using current thermal CVD set-up.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

MENINGKATKAN SIFAT KETEGANGAN BAGI KOMPOSIT POLIPROPILENA DIPERKUAT GENTIAN KARBON DENGAN PENYALUTAN KARBON TIUB NANO

Oleh

SHARIFAH MAZRAH BINTI SAYED MOHAMED ZAIN

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Gentian karbon, apabila digunakan tanpa rawatan permukaan, ia akan menghasilkan komposit yang mempunyai kekuatan ricih antara lamina (ILSS) yang rendah seterusnya menyumbang kepada ikatan lemah antara gentian dan matriks resin. Rawatan penyalutan karbon tiub nano keatas permukaan gentian karbon telah dijalankan untuk meningkatkan ikatan antara muka gentian karbon dan matriks. Rawatan ini dijalankan dengan menumbuhkan karbon tiub nano ke atas permukaan gentian karbon menggunakan kaedah pemendapan wap kimia (CVD). Objektif kajian ini adalah untuk mengkaji gambaran sifat karbon tiub nano yang terbentuk pada keadaan rawatan berbeza, menganalisis kekuatan ricih antara muka (IFSS) gentian karbon terawat, sifat ketegangan dan kestabilan terma komposit gentian karbon terawat dan juga perbandingan dengan gentian karbon tidak dirawat dan gentian karbon komersial. Karbon tiub nano yang terbentuk telah dihasilkan melalui tindak balas wap antara benzena dan ferosena di dalam tiub relau bersuhu tinggi. Suhu tindak balas, kadar alir gas pembawa (hidrogen) dan jumlah ferosena di jalankan pada suhu 700 ^{o}C, 800^{o}C dan 900^{o}C; 100 ml/min dan 300 ml/min; 0.3 g, 0.5 g dan

1.0 g, masing-masing dan masa tindak balas bagi pembentukan karbon tiub nano ditetapkan pada 30 minit. Kajian morfologi mikroskopi karbon tiub nano yang terbentuk dijalankan menggunakan mikroskop elektron imbasan (SEM) dan mikroskop elektron transmisi (TEM) sebelum ia di jadikan komposit. Komposit disediakan dengan campuran lebur polipropilena dan gentian karbon pada kandungan berat peratus berbeza iaitu 2, 4, 6, 8, 10 and 12%. Keputusan menunjukkan karbon tiub nano terbentuk dengan jayanya menyaluti permukaan gentian karbon pada suhu rawatan 800^{o}C and 900^{o}C. Kekuatan ricih antara muka gentian karbon terawat iaitu disaluti karbon tiub nano telah meningkat sebanyak 499% berbanding gentian karbon tidak dirawat. Sifat ketegangan meningkat dengan peningkatan peratus pengisian gentian dari 2 - 10% dan menurun pada 12% kandungan gentian karbon. Dengan penambahan sebanyak 10% gentian karbon terawat ke dalam polipropilena komposit, kekuatan dan modulus ketegangan meningkat sebanyak 36% dan 85%, masing-masing. Komposit gentian karbon terawat mempunyai rintangan lebih tinggi terhadap canggaan, tetapi mempunyai kekuatan yang lebih rendah jika dibandingkan dengan komposit gentian karbon komersial. Kestabilan terma bagi komposit gentian karbon terawat menunjukkan peningkatan berbanding dengan komposit gentian karbon tidak dirawat. Kesimpulannya, penyalutan karbon tiub nano pada parameter 800^{o}C; kadar alir gas hidrogen 300 ml/min dan 1.0 g ferosena telah menunjukkan pembentukan karbon tiub nano yang paling banyak dan kurang bendasing. Ia juga menunjukkan prestasi terbaik bagi kekuatan ricih antara muka, sifat ketegangan dan suhu penguraian tertinggi, 325^{o}C menjadikan ia formula terbaik bagi rawatan ini menggunakan set alat terma CVD yang sedia ada.

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I owe my loving thanks to my husband Syed Mohamad Nazli bin Syed Ahmad, my parents and families for their loving support. Without their encouragement and understanding, it would have been impossible for me to finish this work.

I certify that a Thesis Examination Committee has met on 20 November 2009 to conduct the final examination of Sharifah Mazrah binti Sayed Mohamed Zain on her thesis entitled "Enhancing Tensile Properties of Carbon Fiber-Reinforced Polypropylene Composite using Carbon Nanotube Coating" in accordance with the Universitites and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Putra Malaysia or other institutions.

SHARIFAH MAZRAH SAYED MOHAMED ZAIN

Date:

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATION

ABS	Acrylonitrile butadiene styrene
ASTM	American Society for Testing and Materials
Al_2O_3	Aluminium oxide
Ar	Argon
CCD	Charge coupled device
CF	Carbon fiber
CNFs	Carbon nanofibers
CNTs	Carbon nanotubes
CFPP	Carbon fiber reinforced polypropylene
CFRC	Carbon-carbon fiber reinforced composites
CFRM	Carbon fiber-metal reinforced composites
CFRP	Carbon fiber-polymer matrix composites
CVD	Chemical vapor deposition
Co	Cobalt
C_6H_6	Benzene
E	Modulus of elasticity
EDX	Energy dispersive x-ray
Fe	Iron
$Fe(C_5H_5)_2$	Ferrocene
FRP	Fiber reinforced polymer
GPa	Gega Pascal
H_2	Hydrogen
HRTEM	High resolution transmission electron microscope
IFSS	Interfacial shear stress

ILSS	Interlaminar shear strength
L_c	Critical length
MFI	Melt flow index
Mo	Molybdenum
MW	Molecular weight
MWNTs	Multi-walled nanotubes
Ni	Nickel
PAN	Polyacronitrile
PC	Polycarbonate
PEEK	Polyetheretherketone
PP	Polypropylene
PPS	Polyphenylene sulfide
PS	Polysulfone
RTC	Restrained top loading
SEM	Scanning electron microscope
SFRP	Short-fiber reinforced polymer composites
SiC	Silicon carbide
Si_3N_4	Silicon nitride
SWNTs	Single-walled nanotubes
TiO_2	Titanium dioxide
TEM	Transmission electron microscope
TGA	Thermo gravimetric analysis
VGCF	Vapor grown carbon nanofibers

CHAPTER 1

INTRODUCTION

1.1 Background Study

It had been established in recent years that polymer-based composites reinforced with a small percentage of strong fillers could significantly improve the mechanical, thermal and barrier properties of pure polymer matrix (Mahfuz et al., 2003). When these fillers are rod-shaped, the surface area per particle will be higher than any other shape of fillers. Carbon fibers have extremely high mechanical strength and stiffness in axial direction and because of this, they are considered the most interesting fillers for advanced applications composites (Gordeyev et al., 2001). Composite materials have two major advantages among many others; improved strength and stiffness, especially when compared with other materials on a unit of weight basis. For example, composite materials can be made to have the same strength and stiffness as high-strength steel and yet 70% lighter. Other advanced composite materials such as rural material, yet weigh only 60% as much. Composite materials can be tailored to efficiently meet design requirements of strength, stiffness and other parameters, all in various directions (Jones, 1999).

Good composite performance often depends on the degree of adhesion between the fiber and the resin binder. The physical and chemical properties of carbon fibers play a major role in determining the degree of adhesion between the fiber and the resin matrix. Adhesion is usually controlled by chemical bonding due to functional groups and by mechanical interlocking due to surface morphology. This leads researchers to develop a number of surface treatments that could improve the fiber matrix polymer interfacial bonding. In order to improve the bonding properties of carbon fibers, various surface treatment approaches can be applied.

Carbon fiber surfaces are chemically inactive and must be treated to form surface functional groups that promote good chemical bonding with resin matrix. Surface treaments for carbon fibers are of two types, oxidative and non-oxidative. Oxidative surface treatments produce acidic functional groups on the carbon fiber surface. Non-oxidative surface treament was developed by coating the carbon fiber surface with an organic polymer that has funtional groups capable of reacting with the resin matrix (Mallick, 1993).

One of the non-oxidative surface treatment methods is whiskerization. It was an affective way to increase the shear strength of carbon-epoxy composite materials by 400% (Kowbel et al., 1997). Whiskerization technique on carbon fiber appears to have positive effect in improving the interfacial adhesion between carbon fibers and the matrix (Kowbel et al., 1997; Rebouillat, 1984; Katsuki et al., 1987 and Ismail, 1993). Whiskerization involves growing carbon nanotubes (CNTs) on the surface of carbon fibers. By growing the nanotubes on the surface of carbon fibers, the total surface area would increase and enhance the mechanical interlocking between fibers and resin matrixes. Over a decade, carbon nanotubes have attracted great interest in the scientific field because of their unique structure, remarkable mechanical, thermal and electrical properties and potential applications. Based on their exceptional tensile strength and modulus, CNTs are deemed to be able to improve the tensile properties of the composite material and to increase the fracture energy once a crack is initiated.

A lot of studies and applications had recommended that nanotubes to be grown directly on substrate (carbon fiber) to minimize contact resistance between the nanotubes and the substrate, especially in large area at low cost, which however is still a challenge (Li et al., 2000). There are many techniques in producing CNTs and chemical vapor deposition (CVD) had been found to be efficient and selective for either single-walled or multi-walled carbon nanotubes and had demonstrated several advantages in growing the carbon nanotubes (Zhu et al., 2003). It had been established in recent years that polymer-based composites reinforced with the superior properties of carbon nanotubes (CNTs) could enhance and significantly improve the performance of the polymer matrix and numerous composites.

1.2 Problem Statement

It is well known that fiber-matrix adhesion strength plays an important role on the mechanical properties of fiber-reinforced polymer composites (Mallick, 1993). When load is applied to composites, it will be distributed and transferred through fiber-matrix interfaces. A strong bonding promotes a better involvement of more fibers which increases the strength of composites accordingly. However, carbon fibers usually experience a poor bonding behavior to polymer matrix due to their nature of smoothness and chemical inertness. This had been attributed largely to poor adhesion or weak bonding between carbon fiber surface and matrix molecules. Carbon fibers, when used without any surface treatment, produce composites with low interlaminar shear strength (ILSS) (Zhang et al., 2004). Kowbel and co-worker reported an improvement of 200% - 300% in interlaminar shear strength (ILSS) of CNT-coated carbon fiber-reinforced epoxy composites. CNTs which increase the interfacial area of carbon fibers (Thostensen et al., 2001) provide a larger number of contact points for fiber-matrix bonding which attributed to the improvements in ILSS (Mallick, 1993).

Since carbon fibers produce composites with poor interfacial shear strength when used without any surface treatments, it has led investigators to develop a number of surface treatments (Rebouillat, 1984). The importance of surface treatment is due to the surfaces of carbon fibers that are chemically inactive. Surface functional groups would formed on carbon fibers surface by treatment that would enhanced good bonding with the resin matrix, hence improving the mechanical properties of composites produced. With better mechanical properties of composites, it attracts many manufacturers to develop various types of usage in industrial, recreational and engineering field.

This research intends to study the surface treatment on carbon fibers using one of the surface treatments. The as-received PAN carbon fibers were treated by using the concept of whiskerization. This treatment was done by growing carbon nanotubes directly on carbon fibers using chemical vapor deposition (CVD) to create CNT-coated carbon fibers. Each individual carbon fiber, which is several microns in diameter, is surrounded by carbon nanotubes. The morphology of CNTs grown on carbon fiber substrate was observed at various treatment conditions and the interfacial shear strength of these treated fiber were measured. Although there is much research done on the production of CNTs on carbon fibers, none had studied the tensile behavior of CNT-coated carbon fiber-reinforced polypropylene composites using short fibers. The effect of CNT-coating treatment in the enhancement of tensile properties of the treated carbon composite was studied.

1.3 Objectives of Study

The objectives and scope of study had been clearly defined to achieve the goal of this research and are listed as follow:

1. To study the microscopic morphology of CNTs formation on the surface of carbon fibers by CNT-coating treatment at various treatment conditions.

2. To determine the effect of CNT-coating treatment on carbon fibers by studying the interfacial shear strength (IFSS) of CNT-coated carbon fibers, tensile properties and thermal stability of CNT-coated carbon fiber composites.

3. To investigate the comparison of tensile properties and thermal stability between CNT-coated carbon fiber composites with the commercial carbon fiber composites.

1.4 Scope of Study

The scope of study of this research are as follow:

1. CNT-coating treatment was conducted using CVD method by varying the reaction temperature (700 °C, 800°C and 900°C), hydrogen flow rate (100 ml/min and 300 ml/min) and weight of ferrocene (0.3g, 0.5g and 1.0g). The microscopic morphology of CNTs formation on the surface of carbon fibers was observed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

2. Untreated, CNT-coated and commercial carbon fibers were fabricated into composites by reinforcing them with polypropylene at different fiber content. The carbon fiber content was varied between 2 wt. % and 12 wt. %. The improvement in tensile properties at different treatment conditions and fiber load were determined.

3. The fiber matrix adhesion was assessed by the interfacial shear strength (IFSS) test and the thermal stability of untreated and CNT-coated carbon fiber composites was determined by its onset degradation temperature.

1.5 Thesis Structure

The thesis structure is organized into five chapters. Chapter Two consists of literature review, which encompasses background information and review of previous work done which is related to carbon fibers, carbon nanotubes growth by CVD and using carbon fiber as fillers in a polymer based matrix. It also includes fundamental theory regarding mechanical properties of carbon fiber reinforced polymer matrix composites. In Chapter Three, the type of materials incorporated, instruments and apparatus used, formulas as well as the procedure for sample preparation is presented. Detailed results of CNT-coating treatment on carbon fibers, morphology study, and experimental data obtained are presented in Chapter Four with discussions on data analysis and interpretation. Finally, Chapter Five concludes the overall work by reporting the important findings from the research done and recommendations for future work.

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